Geoscience Frontiers 8 (2017) 65–80

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Contents lists available at ScienceDirect

China University of Geosciences (Beijing)

Geoscience Frontiers

journal homepage: www.elsevier.com/locate/gsf

Research paper

Mineralogical and geochemical characteristics of Miocene pelitic sedimentary rocks from the south-western part of the Pannonian Basin System (Croatia): Implications for provenance studies

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ARTICLE INFO

Article history:
Received 23 July 2015
Received in revised form
12 November 2015
Accepted 20 November 2015
Available online 25 December 2015

Keywords:
Mineralogy
Chemical composition
Miocene
Provenance
Discriminant function analysis
Pannonian Basin System

ABSTRACT

Fifty-two samples of Miocene pelitic sedimentary rock from outcrops on Medvednica, Moslavačka Gora and Psunj Mts., and boreholes in the Sava Depression and the Požega Sub-depression were investigated. These sediments formed in different marine (with normal and reduced salinity), brackish, and freshwater environments, depending on the development stage of the Pannonian Basin System. Carbonate minerals, clay minerals and quartz are the main constituents of all pelitic sedimentary rocks, except in those from Moslavačka Gora Mt in which carbonate minerals are not present. Feldspars, pyrite, opal-CT, and hematite are present as minor constituents in some rocks. Besides calcite, dependent on the sedimentary environment and diagenetic changes, high-magnesium calcite, aragonite, dolomite and ankerite/Ca-dolomite are also present. Smectite or illite-smectite is the main clay minerals in the samples. Minor constituents, present in almost all samples, are detrital illite and kaolinite. In some samples chlorite is also present in a low amount. Major elements, trace elements and rare earth elements patterns used in provenance analysis show that all analysed samples have a composition similar to the values of the upper continental crust (UCC). The contents of major and trace elements as well as SiO_2/Al_2O_3, K_2O/Al_2O_3, Na_2O/K_2O, Eu/Eu*, La/Sc, Th/Sc, La/Co Th/Co, Th/Cr, Ce/Ce* and LREE/HREE ratios, show that the analysed pelitic sedimentary rocks were formed by weathering of different types of mostly acidic (silicic), i.e. felsic rocks.

1. Introduction

Pelitic sedimentary rocks, comprising marls, clayey limestones and silty marls originated in different marine, brackish and freshwater environments depending on the development of the Pannonian Basin System (PBS) (Fig. 1). The depositional environment and the pertaining stratigraphic unit of the sediments are known from palaeontological data.

One of the main constituents of pelitic sedimentary rocks is clay minerals which can be used as indicators of climate. Formation of clay minerals is related to the type of the parent material, climate and chemical conditions of their occurrence. Previous studies on the provenance of Miocene sediments in the southwestern part of the PBS were mostly done on the sandy fraction and were based on the modal analyses of the light and heavy minerals fraction (Šćavničar, 1979; Šimunić and Šimunić, 1987; Kovačić, 1999, 2004; Kovačić et al., 2004; Kovačić and Grizelj, 2006; Kovačić et al., 2009, 2011), while the provenance research based on the chemical composition of pelitic sedimentary rocks was performed only on the upper Miocene marls from Zagorje Basin (Grizelj et al., 2007). Analysing the Miocene sands and gravels of Dilj Gora Mt. Kovačić et al. (2011) concluded that the Inner Dinarides were the main source area for lower Miocene detritus. Most of detritus during the middle Miocene was derived from both the Inner Dinarides and locally uplifted Slavonian Mts., while upper Miocene clastic detritus is mainly of Alpine-Carpathian provenance. Ščavnićar (1979) noted a significant difference in the modal composition of the Abichi and Banatica sandstones from the Sava Depression, compared to older Miocene sediments. She believed that Miocene sediments of the middle Miocene to early part of the late Miocene have derived from a closer source area, while the younger sediments have derived from more distant areas, such as

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Peer-review under responsibility of China University of Geosciences (Beijing).

http://dx.doi.org/10.1016/j.gsf.2015.11.009

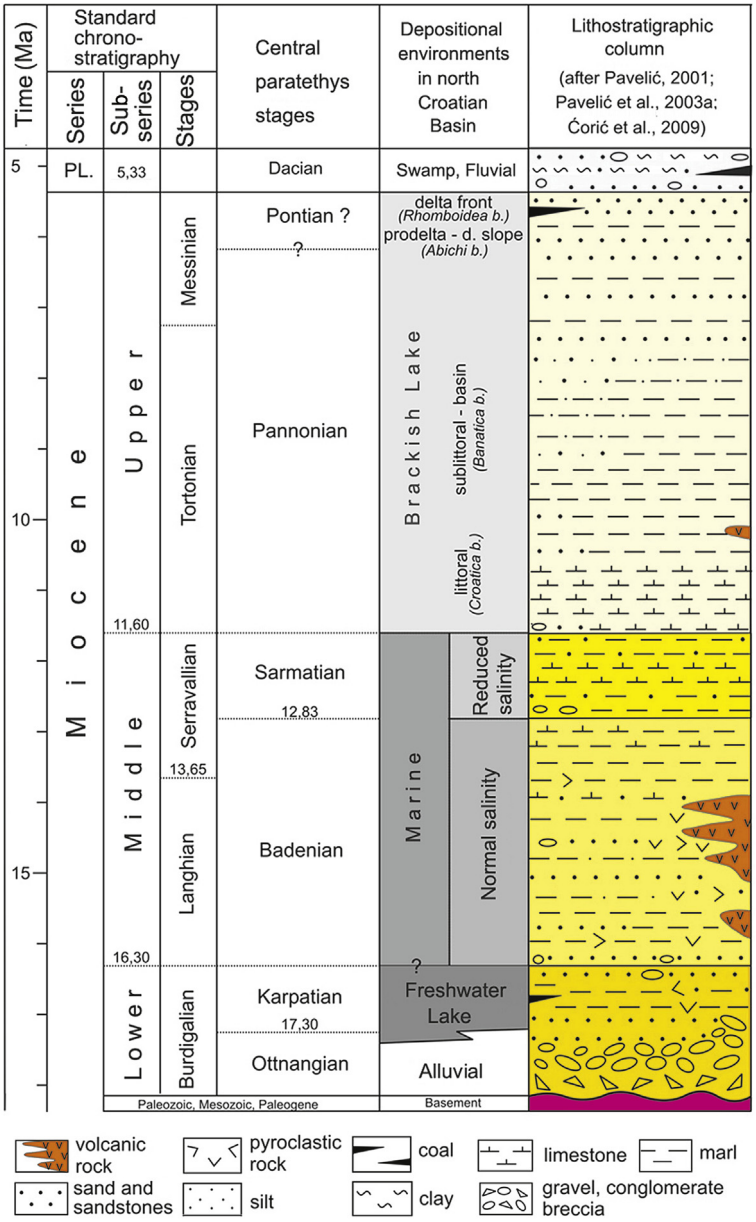

Figure 1. Geological time scale of Central Paratethys correlated with the standard geological time scale (after Harzhauser and Piller, 2007). Depositional environments in North Croatian Basin (after Pavelić, 2001; Pavelić et al., 2003a; Ćorić et al., 2009).

the Alps. Mutić (1981) detected the good correlation between the composition of the heavy mineral fraction and the pertaining biostratigraphic unit for Miocene beds of the northwestern part of Hrvatsko Zagorje. Later research on the provenance of the sand fractions of the upper Miocene sediments also indicated the origin of the material from the Eastern Alps (Šimunić and Šimunić, 1987; Kovačić, 1999; Kovačić et al., 2004, 2011). According to the provenance research of the upper Miocene sediments, Kovačić and Grizelj (2006) concluded that older lithostratigraphic units reflect the local origin of the material, while the younger sediments originated from dominantly siliciclastic sedimentary and metamorphic rocks of the Eastern Alps, and in a lesser amount of the Western Carpathians. The chemical composition of the upper Miocene pelitic sedimentary rocks from Hrvatsko Zagorje also indicates the Alpine provenance of the clastic material (Grizelj et al., 2007).

The aim of this paper is to reveal the provenance of pelitic sedimentary rocks from the southwestern part of the PBS based on their chemical characteristics and to compare the results with those obtained from the mineral composition of the sand size fraction (Šimunić and Šimunić, 1987; Kovačić, 1999; Kovačić et al., 2004). Additional aim is to determine the optimum criteria for separating the previously defined sedimentary environments of Miocene pelitic sedimentary rocks of the SW portion the PBS using the multiple discriminant analysis based on the chemical composition of their deposits.

2. Geological settings

The Pannonian Basin System (PBS) represents one of the Mediterranean back-arc basins. It comprises the biggest part of the Central Paratethys, a sedimentation area that, during the

Miocene lost and re-established connections with the Mediterranean and the Indo-Pacific Ocean on several occasions. PBS is surrounded by the Alpine, Dinaric and Carpathian mountain belts (Fig. 2) and includes a number of different-sized, deep depressions (sub-basins) separated by comparatively shallow complex of basement rocks (Horváth and Royden, 1981; Royden, 1988). The formation of this back-arc basin started in the early Miocene with continental collision and subduction of the European Plate beneath the Apulian Plate. The development of the PBS took place in two phases. The first (syn-rift) phase of basin development was characterized by tectonic thinning of the crust and isostatic subsidence, while the second (post-rift) phase was marked by subsidence caused by the cooling of the lithosphere (Horváth and Royden, 1981; Royden et al., 1983; Royden, 1988). According to Pavelić (2001) in the southwestern part of the PBS the syn-rift phase lasted from the Ottnangian to the middle Badenian, while the post-rift phase extended from the middle Badenian to the end of the Pontian.

The studied area is located in the northern Croatia in southwestern part of PBS (North Croatian Basin; Pavelić, 2001) (Fig. 2). It extends from the eastern part of the Medvednica Mt. over a narrow area along the Sava River (Sava Depression) and the northern slopes of the Moslavačka Gora Mt., to the southeastern slopes of the Psunj Mt. and the Požega Valley (Požega Sub-depression).

The Sava Depression, as a sub-basin of the PBS, is located in its SW part. It represents the deepest basin sediment sequence and was investigated in more detail in this paper. The Neogene deposits of the SW part of the PBS overlie the Palaeozoic–Mesozoic–Paleogene basement consisting of various magmatic, metamorphic and sedimentary rocks (Šikić et al., 1979; Šparica et al., 1980; Basch, 1983; Šparica and Buzaljko, 1984; Korolija et al., 1986; Jamičić et al., 1987, 1989; Pamić, 1998). The thickness of both Neogene and Quaternary deposits in the Sava Depression exceeds 5.0 km (Saftić et al., 2003), in the Požega Sub-depression the thickness is around 2.7 km (Najdenovski, 1988) while in the surrounding mountains it can be only a few tens of meters.

The evolution of Neogene sedimentation in the Croatian part of the PBS was described in detail by several authors (Najdenovski, 1988; Avanić et al., 1995; Pavelić et al., 1998; Pavelić and Kovačić, 1999; Vrsaljko, 1999; Barić et al., 2000; Lučić et al., 2001; Pavelić, 2001; Vrbanac, 2002; Avanić et al., 2003; Pavelić et al., 2003a,b; Saftić et al., 2003; Pavelić, 2005; Herak, 2006; Kovačić and Grizelj, 2006; Vrsaljko et al., 2006; Ćorić et al., 2009; Hajek-Tadesse et al., 2009; Grizelj et al., 2011; Kovačić et al., 2011).

Deposition of the syn-rift sediments began in the early Miocene, unconformably on the tectonised Paleozoic–Mesozoic crystalline basement. These oldest sediments are represented by breccias, conglomerates, sandstones and marls deposited in alluvial and freshwater lake environments (Fig. 1). At the beginning of the middle Miocene a connection with marine areas was established. Marine sandstones, marls and tuffs were deposited continuously on lower Miocene sediments. Syn-rift sedimentation ended in the middle Miocene. During the middle Miocene, marine conditions of sedimentation continued. Dominant sediments were lithothamnium limestones, sandstones and marls intercalated by pyroclastic rocks resulted from occasional volcanic activity. In the Sarmatian the connections of the PBS with marine areas were significantly reduced (Fig. 1). Due to this changes marls and sandstones deposited in environments of reduced salinity, mostly continuously on the Badenian deposits. The brackish Lake Pannonian was formed at the beginning of the late Miocene, due to isolation trends affecting the PBS. Upper Miocene sediments, known as Croatica beds are composed of thin-bedded clayey limestones and marls with occasional intercalations of calcareous sands deposited in the shallow lake environment of low salinity. The contact with the underlying Sarmatian deposits is mostly sharp and conformable. Sedimentation of marls and sandstones gradually began during the late Miocene. Upper Miocene beds deposited in deep-water brackish environment are known as Banatica beds. Going to the end of late Miocene the PBS became shallower and was gradually filled by sands due to the progradation of deltaic systems forming the Abichi beds which overlie Banatica beds. Abichi beds were deposited in a prodelta–deltaic slope lacustrine environment.

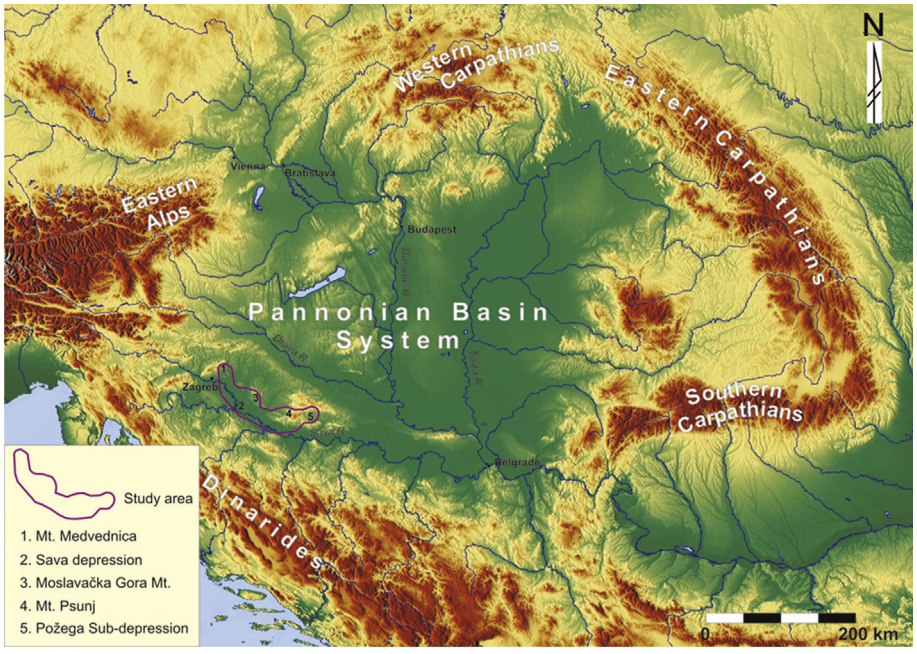

Figure 2. Pannonian Basin System and its surroundings with indicated locations of the study area.

They consist of marls, silts and sands. At the end of late Miocene, Rhomboidean sands and silts deposited in a delta front in the shallow brackish lacustrine environment.

Pliocene and Quaternary sediments consist of clays, sands and gravels which were deposited in the freshwater lake, swamp and fluvial environments.

3. Materials and methods

Mineralogical and geochemical analysis was performed on 52 Miocene samples (Table 1). Thirty-two samples were from boreholes in the Sava Depression (27) and the Požega Sub-depression (5), while 20 samples were collected from outcrops on Medvednica (13), Moslavačka Gora (2) and Psunj Mountains (5).

X-ray powder diffraction (XRPD) patterns were recorded on random and oriented mounts of the fraction <2 μm of air dried material, and after glycol treatment, heating to 400 and 550 °C (Starkey et al., 1984) using a Philips vertical X-ray goniometer (type X'Pert) equipped with a Cu tube and graphite crystal monochromator. The experimental condition were as follows: 45 kV, 40 mA, X-celerator detector, primary beam divergence 1/2°, antiscatter slit 1°, detector antiscatter slit 5.5 mm.

Illite-smectite (I-S) type and the smectite ratio in I-S were determined by peak position methods (Środoń, 1981, 1984). The semi-quantitative analysis was performed according to Schultz (1964).

Chemical analyses of samples were performed in ACME Analytical Laboratories LTD (www.acmelab.com) in Vancouver (Canada). The major elements content was determined by inductively coupled plasma emission spectroscopy (ICP-ES) after a $LiBO_2$ fusion. Trace elements were measured on an inductively coupled plasma mass spectrometer (ICP-MS). Rare earth and incompatible

Table 1
Description of analysed samples (index, type of sediment and colour, depth, age – Central Paratethys regional stages, depositional environment).

Sample		Description of samples	Depth (m)	Age	Environment Group
Mt. Medvednica	Vej-III 1	Gray marl		Middle Miocene	M
	Vej-III 11/1	Brown silty marl		Middle Miocene	M
	Vej-III 65	Yellowish to brownish marl		Middle Miocene	M
	MeB-I 1/1	Brown, laminated marl		Middle Miocene	MRS
	MeB-I 7/4	Gray to brown marl		Late Miocene	B
	MeB-I 10/4	Gray marl		Late Miocene	B
	Vug-I 1	Yellowish, platy, clayey limestone		Late Miocene	B
	Vug-I 12/1	Laminated marl		Middle Miocene	MRS
	Vug-I 14/1	Clayey limestone		Late Miocene	B
	DOr-III 7/1	Light-brown marl		Middle Miocene	MRS
	DOr-I 17/1	Light-brown silty marl		Middle Miocene	MRS
	BDl-I 4/2	Grayish to brownish marl		Late Miocene	B
	Jal-I 3/8	Grayish to brownish marl		Late Miocene	B
Sava Depression	Gj-1-1	Light-gray silty marl	839–840.5 (I)	Late Miocene	B
	Gj-1-2	Light-gray silty marl	872–879 (I)	Late Miocene	B
	Gj-1-3	Laminated, dark to light-gray silty marl	937–943.5 (II)	Middle Miocene	MRS
	Gj-1-4	Clayey, calcareous silt	1455–1460.64 (II)	Middle Miocene	M
	Gj-1-5	Clayey, calcareous silt	1839–1845 (VI)	Early Miocene	F
	Gj-1-6	Dark-gray silty marl	1928–1933 (V)	Early Miocene	F
	Gj-1-7	Dark-gray to reddish silty marl	2131–2133 (I)	Early Miocene	F
	DJ-1-1	Changes sandstone and marls	2438–2442 (IV)	Late Miocene	B
	DJ-1-2	Black to dark-gray silty marl	3034–3039 (V)	Late Miocene	B
	DJ-1-3	Black silty marl	3230–3234 (III)	Late Miocene	B
	DJ-1-4	Black silty marl	3295–3297 (II)	Late Miocene	B
	DJ-1-5	Black silty marl	3450–3451 (I)	Middle Miocene	M
	DJ-1-6	Black to dark-gray silty marl	3518–3520 (I)	Middle Miocene	M
	DJ-1-7	Black to dark-gray silty marl	3831–3833 (I)	Middle Miocene	M
	DJ-1-8	Dark-gray silty marl	4230–4232 (II)	Middle Miocene	M
	DJ-1-9	Dark-gray silty marl	4606–4609 (I)	Middle Miocene	M
	DJ-1-10	Dark-gray silty marl	4821–4825 (II)	Middle Miocene	M
	DJ-1-11	Dark-gray silty marl	5000–5003 (I)	Middle Miocene	M
	Mah-1-1	Brown silty marl	1562.4–1565.7 (III)	Late Miocene	B
	Mah-1-2	Gray silty marl	1859.9–1865.5 (II)	Middle Miocene	M
	Lak-1-1	Gray marl with remains of plants	1077–1079.5 (I)	Middle Miocene	M
	Lak-1-2	Gray marl	1200–1204 (IV)	Middle Miocene	M
	Lak-1-3	Dark-gray marl	1247.5–1251.4 (II)	Middle Miocene	M
	JeD-3-1	Dark-gray clayey limestone	2403–2404 (I)	Late Miocene	B
	JeD-3-2	Dark-gray to black clayey limestone	2822–2823.5 (I)	Middle Miocene	M
	Žu-256D-1	Dark-gray to black clayey limestone	2257–2261 (I)	Middle Miocene	M
	Žu-256D-2	Dark-gray to black clayey limestone	2362–2366.5 (III)	Middle Miocene	M
Moslavačka Gora Mt.	Suh-I 1	Gray silty clay		Late Miocene	B
	Vrt-I 1	Light to dark-gray clay		Middle Miocene	M
Mt. Psunj	Ba-I 1/2	Brown, laminated marl		Middle Miocene	MRS
	Ba-I 2/2	Yellowish, clayey limestone		Middle Miocene	MRS
	Ba-I 19/1	Yellowish, clayey limestone		Late Miocene	B
	Pav-I 1	Gray marl		Late Miocene	B
	Pav-I 2	Gray marl		Late Miocene	B
Požega Sub-depression	Tek-1-1	Light-gray silty marl	577–583 (V)	Late Miocene	B
	Tek-1-2	Light-gray silty marl	948–952 (II)	Late Miocene	B
	Tek-1-3	Light-gray silty marl	1180.6–1185.5 (V)	Late Miocene	B
	Tek-1-4	dark-gray silty marl	1450.5–1452.5 (II)	Late Miocene	B
	Tek-1-5	Gray calcareous marl or clayey limestone	1521–1524 (II)	Late Miocene	B

F–freshwater environment, M–marine environment, MRS–marine environment with reduced salinity, B–brackish.

elements were determined after $LiBO_2$ fusion, while the noble and base metals were determined after aqua regia digestion.

Provenance analyses were performed following the results of chemical analysis of major, trace and rare earth elements. For the analysis three component diagrams based on the elemental ratios were used.

For the reconstruction of provenance on the basis of the major elements content diagrams proposed by Roser and Korsch (1986, 1988) and SiO_2/Al_2O_3, K_2O/Al_2O_3 and Na_2O/K_2O ratios were applied.

The diagram proposed by Roser and Korsch (1986) for the reconstruction of geotectonic settings for sandstones and muds is based on a comparison of the K_2O/Na_2O and SiO_2 contents. Because analysed pelitic sedimentary rocks usually contain a substantial amount of carbonates, their composition is recalculated to 100% after subtraction of CaO and appropriate loss on ignition (LOI) contents. Determination of possible source rocks was made using a diagram based on discriminant functions proposed by Roser and Korsch (1988). To avoid the problem of contamination of the silicic and carbonate components by secondary precipitation and biogenic origin in the samples, the oxide/Al_2O_3 ratios diagram is used.

For the analysis of provenance based on trace and rare earth elements (REE) content elemental ratios dependant on provenance like La/Co, Th/Co, Th/Sc, Th/Cr, Eu/Eu* [$Eu^* = Tb\times(Sm/Tb)^{-2/3}$], $(La/Lu)_{cn}$, LREE/HREE, the sum of the rare earth elements (ΣREE) and diagrams La-Th-Sc, Th-Sc-Zr/10, Th/Co–La/Sc and Th/Sc–Cr/Th proposed by Bhatia and Crook (1986), Cullers (1994, 2002) and Totten et al. (2000) were used.

Multiple discriminant analysis of pelitic sedimentary rocks was performed in order to determine the optimum criteria for separating the previously defined sedimentary environments. According to the depositional environment the analysed 52 samples were classified into four groups: (1) marine (M), (2) marine environment of reduced salinity (MRS), (3) brackish (B) and (4) freshwater (F) (Table 1). Analyses were based on the content of main element oxides (SiO_2, Al_2O_3, Fe_2O_3, MgO, CaO, Na_2O, K_2O, TiO_2, Cr_2O_3, P_2O_5, MnO), total C (TOT/C), total S (TOT/S) and trace elements (LREE, HREE, Y, Hf, Zn, Sc, Zr, Th, Ga, Rb, Ni, Pb, Cu, In, As, Hg, Mo, Cs, Sn, W, Ta, Nb, Sr, Ba).

4. Results

4.1. Mineralogy

The mineralogical composition of Miocene pelitic sedimentary rocks is given in Table 2. The main components of the Miocene pelitic sedimentary rocks are carbonate minerals, clay minerals, together with ubiquitous quartz. Some samples contain smaller amounts of feldspar, pyrite, opal-CT and hematite. Calcite content of the surface pelitic sedimentary rocks ranges from 8 to 85 wt.% while in the borehole sediments it is between 3 and 70 wt.%. Clay mineral content ranges from 9 to 67 wt.% and 15 to 65 wt.% in surface pelitic sedimentary rocks and boreholes, respectively. As for the outcrops (Medvednica, Moslavačka Gora and Psunj Mts.), in the less than 2 μm fraction the predominant clay minerals are smectite and illite-smectite (R0 type) with >85 wt.% of smectite component. Small amount of illite and kaolinite is regularly present, while chlorite is present only in some samples. The mineral composition of pelitic sedimentary rocks deposited in the Sava Depression and Požega Sub-depression are considerably different from the stratigraphically equivalent surface sediments. Established differences of the mineral content are the result of diagenetic changes caused by the increase of temperature and depth (Grizelj et al., 2011). The main components in the <2 μm fraction of pelitic sedimentary rocks from boreholes, in greater depths are illite and chlorite, while the smectite and illite-smectite (R0, R1, R > 1) amounts decrease. Simultaneously with the increase of the illite and chlorite amounts, the content of quartz increases. The increase of illite, quartz and chlorite is a result of the smectite illitisation process.

4.2. Chemical composition

The chemical composition and element ratios of samples are given in Supplemental Table. The results show that the content of the main elements of the samples varies. Differences in the content of the main elements are the result of the changes of mineral composition of the samples (Table 2). Fig. 3 represents the REE plots of samples normalized to chondrite (Nakamura, 1974). All samples show LREE > HREE and negative Eu-anomaly which is in accordance to the Eu/Eu* ratio. Fig. 4 shows positive correlations of SiO_2, Fe_2O_3, MgO, Na_2O, TiO_2, K_2O and Cr_2O_3 with Al_2O_3, while CaO is strongly negatively correlated. In Fig. 5, Na_2O is positively correlated with SiO_2, while Cs, V, Ni and Rb are positively correlated with Al_2O_3.

5. Discussion

5.1. Mineralogy

Carbonate minerals are present in all analysed pelitic sedimentary rocks except in samples from Moslavačka Gora Mt. (Table 2). The sediments originated in different depositional environments: either freshwater, marine, marine environment with reduced salinity, or brackish (Vrsaljko, 1999; Avanić et al., 2003; Pavelić et al., 2003b; Kovačić et al., 2004; Vrsaljko et al., 2006; Kováč et al., 2007; Ćorić et al., 2009; Kovačić et al., 2011). As a consequence, the origin of the carbonate component in these samples varies. The most common carbonate mineral is calcite. Some samples contain aragonite and high-magnesium calcite. Dolomite is subordinate to abundant in some samples from the surface. In the samples from the boreholes the excess-Ca dolomite/ankerite is also present together with dolomite. Calcite and aragonite are of biogenic and/or chemical origin. The type of carbonate as well as its morphology depend on the temperature of the water in which it is generated, together with the concentration of Ca and Mg ions in the solution, salinity and pressure of CO_2 (Rao, 1996). While calcite can arise in different environments, aragonite and high-magnesium calcite usually occur in the warm, shallow marine environments by direct precipitation from seawater or from skeletons of various organisms (Lippmann, 1973; Rao, 1996; Chang et al., 1998). Aragonite is mainly present in the marine environment with reduced salinity, and sporadically in the marine sediments. Middle Miocene sediments are characterized by significant amount of fauna remnants. It is assumed that most of the carbonate components in the samples are of biogenic origin, with smaller portion which could arise by precipitation from water. It is known that during the Badenian the southwestern part of the PBS was covered by sea (Kováč et al., 2007). In the Sarmatian, the salinity of the seawater began to reduce (Vrsaljko, 1999; Vrsaljko et al., 2006) followed by the reduction of the Mg/Ca ratio. Therefore, it can be presumed that aragonite should be more abundant in Badenian sediments. On the contrary, aragonite in Badenian sediments is less abundant compared to Sarmatian sediments. Preservation of aragonite in the Sarmatian sediments could be a consequence of the presence of clay minerals in all the samples. Clay minerals and lamination of sediments could contribute to conservation of aragonite as seen in Sarmatian sediments (Tišljar, 2001).

Dolomite, which is present in a small quantity in the samples, probably has a local origin. This is supported by the weak resistance of dolomite to alterations preventing it from surviving longer

Table 2
Semi-quantitative mineral composition (in wt.%) obtained by XRD analysis according to the procedure described by Schultz (1964). Clay minerals content was determined in the <2 μm fraction while the content of other minerals was determined on bulk samples.

	Samples	Qtz	Clm	Cal	Arg	Dol	Ank/Ca-Dol Ca-Dol	Kfs	Pl	Py	Hem	OCT	S	I-S (R0)	I-S (R < 1)	Ill/Ms	K	Chl
Mt. Medvednica	Vej-III 1	12	52	33					3					***		*		
	Vej-III 11/1	6	20	67		5			2					***		*		+
	Vej-III 65	4	19	71					5					***		**	+	+
	MeB-I 1/1	10	40	10^{m}	36			+	1				***			*	*	
	MeB-I 7/4	6	21	71					2				***			**	*	+
	MeB-I 10/4	6	28	59		4		+	2					***		*	*	+
	Vug-I 1	3	13	84										***		*	*	
	Vug-I 12/1	15	63	8^{m}								14		***		**	*	+
	Vug-I 14/1	4	21	75										***		*	*	
	DOr-III 7/1	11	41	45		1			2					***		*	+	
	DOr-I 17/1	4	16	80										***		*	*	
	BDl-I 4/2	12	52	11		20			5				**			**		*
	Jal-I 3/8	10	32	56					2					***		**	*	+
Sava Depression	Gj-1-1	6	23	11^{m}	54	2	2		2					***		**	*	+
(Grizelj et al., 2011)	Gj-1-2	4	15	16	59	2	3			1				***		**	*	*
	Gj-1-3	11	46	10		2				17		14		***		**	*	
	Gj-1-4	20	40	30		3			5	2				***		**		*
	Gj-1-5	11	65	12					12						***	**	*	*
	Gj-1-6	9	61	3		7			9	11					**	**		*
	Gj-1-7	23	49	11					15		2				***	**		*
	Dj-1-1	10	50	4		29			7						**	**		**
	Dj-1-2	4	34	56		3			3						*	***		**
	Dj-1-3	3	29	56		9			1	2					**	***		*
	Dj-1-4	5	22	63		3	3		2	2					**	***		*
	Dj-1-5	5	17	70			2		3	3					*	***		
	Dj-1-6	9	17	58			6		6	4					**	***		
	Dj-1-7	10	28	50			5		3	4					**	**		
	Dj-1-8	14	29	45			3		6	3					**	***		
	Dj-1-9	15	38	37			2		7	1					*	***		**
	Dj-1-10	21	42	25		2			8	2					*	***		**
	Dj-1-11	21	54	9			4		11	1					*	***		**
	Mah-1-1	12	54	20		8			6						*	**	**	*
	Mah-1-2	12	18	65			2		2					***		**		*
	Lak-1-1	3	21	70		4				2				*		**	**	*
	Lak-1-2	5	26	42			24		3					**		**	*	*
	Lak-1-3	13	45	30			8		4					***		**		*
	JeD-3-1	5	19	72			2		2						**	***		
	JeD-3-2	12	19	41		10			8	5					**	***		
	Žu-256D-1	13	34	29	5	2			3	14				***		**	*	
	Žu-256D-2	10	25	49			8		3	5				**		**	*	
Moslavačka Gora Mt.	Suh-I 1	23	65					3	2					***		**	*	
	Vrt-I 1	21	57			1		2	15					***		*	*	
Mt. Psunj	Ba-I 1/2	16	67	10^{m}	3			2	2				***			**	*	
	Ba-I 2/2	3	9	2	85				1					***		**	*	
	Ba-I 19/1	1	10	2	87			+	1					***		**	*	
	Pav-I 1	5	18	73		1			2	1			***			**	*	*
	Pav-I 2	6	20	71				1	1	1			***			**	*	*
Požega	Tek-1-1	8	27	62		3								***		**	*	*
Sub-depression	Tek-1-2	9	25	63		+			2					***		**	*	*
	Tek-1-3	4	19	75										***		**	*	*
	Tek-1-4	5	29	66										**		**	*	*
	Tek-1-5	4	24	67			3		2						**	**	**	+

Qtz – quartz, Clm – Clay minerals, Cal – calcite, ^{m} – high-magnesium calcite, Arg – aragonite, Dol – dolomite, Ank/Ca-Dol – ankerite/high-calcium dolomite, Kfs – Potassium feldspar, Pl – plagioclase, Py – pyrite, Hem – hematite, OCT – opal-CT, S – smectite, I-S (R0) – illite-smectite R0 type, I-S (R > 1) – illite-smectite R > 1 type, Ill/Ms – illite and/or muscovite, K – kaolinite, Chl – chlorite, *** – dominant (>50 wt.%), ** – abundant (20–50 wt.%), * – subordinate (1–20 wt.%), + – traces (<1 wt.%), ** – two types of I-S.

transport and by the fact that dolomite is well represented in the Mesozoic sediments on Medvednica and Slavonian Mts. (Šikić et al., 1979; Šparica et al., 1980; Basch, 1983; Jamičić et al., 1987, 1989). In the samples from the boreholes dolomite and excess Ca-dolomite/ankerite are present. Ankerite in sedimentary rocks can be result of diagenetic processes and hydrothermal alteration. In some cases, the presence of organic matter is necessary for its formation (Chamley, 1989; Chang et al., 1998).

In the sediments from the surface in the <2 μm fraction the main components are I-S (R0) and/or smectite. Illite and kaolinite occur in a lesser amount. In some of the samples there is a small amount of chlorite. Most of clay minerals have a detrital origin. Chlorite, illite and interlayered I-S are formed directly from disintegrating intrusive and metamorphic rocks, while poorly to moderately crystallized smectites indicate alteration in a humid environment and locally increased volcanic activity (Chamley, 1989). Although no traces of volcanic activity were determined in the analysed sediments, intensive volcanic activity in the investigated area during the early and middle Miocene has been investigated and indicated in previous studies (Šikić et al., 1979; Basch, 1983; Jamičić et al., 1987, 1989; Pamić et al., 1995; Šikić, 1995; Pamić, 1997; Barić et al., 2000; Avanić et al., 2003; Bajraktarević and Pavelić, 2003; Kováč et al., 2003, 2007; Saftić et al., 2003). Occasional occurrences of the late Miocene volcanism were also

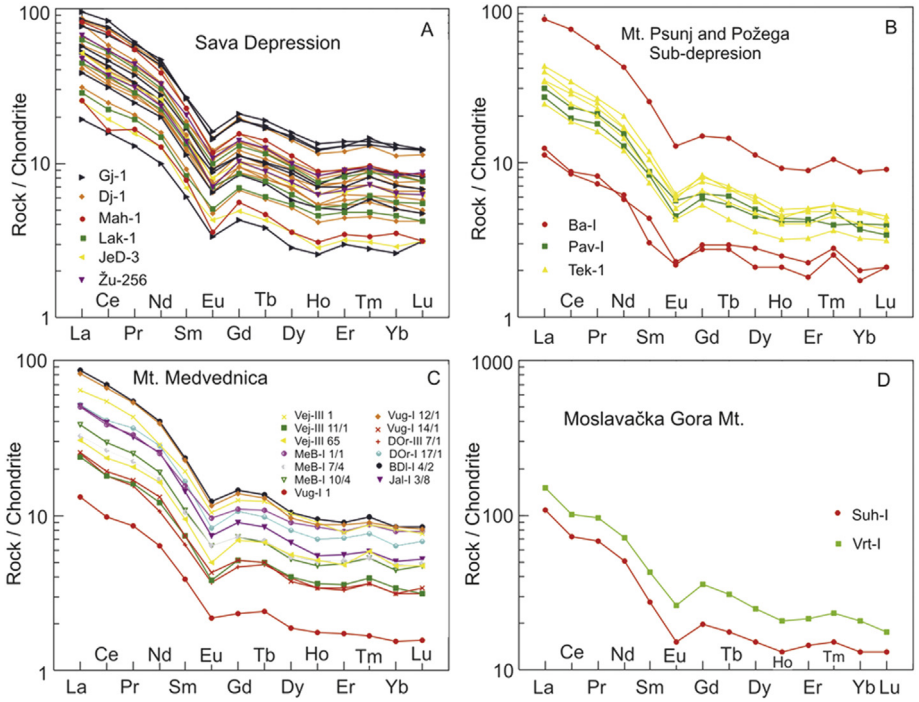

Figure 3. Rare earth element plots of samples from (A) Sava Depression, (B) Mt. Psunj and Požega Sub-depresion, (C) Mt. Medvednica and (D) Moslavačka Gora Mt., all normalized to chondrite after Nakamura (1974).

reported in the wider area of the PBS (Balogh et al., 1983; Szabó et al., 1992; Pamić et al., 1995; Pamić, 1997; Harangi, 2001). The occurrence of smectite in the analysed samples may be linked to the volcanic material from some of these events. Material from volcanic eruption can be transported over long distances. Furthermore, smectite could arise from volcanic material re-deposited from older formations.

Most of smectite occurs in interlayer I-S (Weaver, 1989). In the analysed samples from the surface the majority of I-S is the R0 type containing more than 85% smectite layers. In the surface conditions illitisation of smectite is a consequence of repeated wetting and drying and/or increased pH values, potassium availability and longer exposition to elevated temperatures (Chamley, 1989; Weaver, 1989; Środoń, 2007). Smectite and illite are abundantly represented in the sediments deposited during the higher salinity in comparison to kaolinite (Brooks and Ferrell, 1970; Weaver, 1989). In the samples from the surface no difference exists between the illite and smectite content on the one side and kaolinite on the other in relation to the sedimentary environment. A part of the illite in the samples, except where originated in the process of illitisation, is probably of detrital origin. Chlorite is poorly resistant to chemical weathering. It occurs as a detrital component in the environments where chemical weathering is subordinate (Chamley, 1989; Weaver, 1989). Such areas are characterized by a cooler climate, steep relief, intense erosion and rapid sediment transport. According to previous palaeoclimate studies (Böhme, 2003), during the Miocene humid climate prevailed in Central Europe, except in colder periods of the late Badenian. The small amount of chlorite in Miocene deposits is possibly a result of chemical alteration.

In the pelitic sedimentary rocks from boreholes in the <2 μm fraction, main constituents are illite and I-S. Chlorite and kaolinite are subordinate constituents. The content of illite and chlorite generally increases with depth, while the content of I-S decreases (Table 2). Diagenetic changes in clay minerals from the Sava Depression are described in detail in the Grizelj et al. (2011).

5.2. Chemical composition

5.2.1. Inferred tectonic setting

For the determination of tectonic settings both diagrams proposed by Roser and Korsch (1986) and Bhatia and Crook (1986) were used. Most of the analysed samples plot in the field of the Active Continental Margin, while some samples fall into the field of the Oceanic Island Arc (Fig. 6).

According to Roser and Korsch (1986) the active continental margin represents quartz-intermediate sediments derived from tectonically active continental margins on, or adjacent to, the active plate boundaries. This category comprises the complex active margins, including material derived from the continental margin magmatic arc (deposited in a variety of basin settings such as fore-arc, back-arc, intra-arc and trench) and material derived from uplifted areas associated with strike-slip faults and deposited in a pull-apart basin.

Bhatia and Crook (1986) proposed the La-Th-Sc and Th-Sc-Zr/10 discriminatory plots which served as a basis for the similar plots in this work (Fig. 7). According to these, Miocene pelitic sedimentary rocks plot close to the average composition of the upper continental crust (Taylor and McLennan, 1985) and more or less within the field of the Continental Island Arc. According to Bhatia and Crook (1986) the Continental Island arc is an inter-arc, fore-arc or back-arc basin, adjacent to a volcanic-arc developed on a thick continental crust or thin continental margins.

The inferred tectonic position is consistent with the belief that the PBS as one of the Mediterranean back-arc basins that existed from the Miocene to the Pliocene (Horvath and Royden, 1981; Royden, 1988).

5.2.2. Provenance

5.2.2.1. Major elements. Most analysed pelitic sedimentary rocks in the discrimination diagram of Roser and Korsch (1988) (Fig. 8) fall into the field which indicates that the materials originate from the

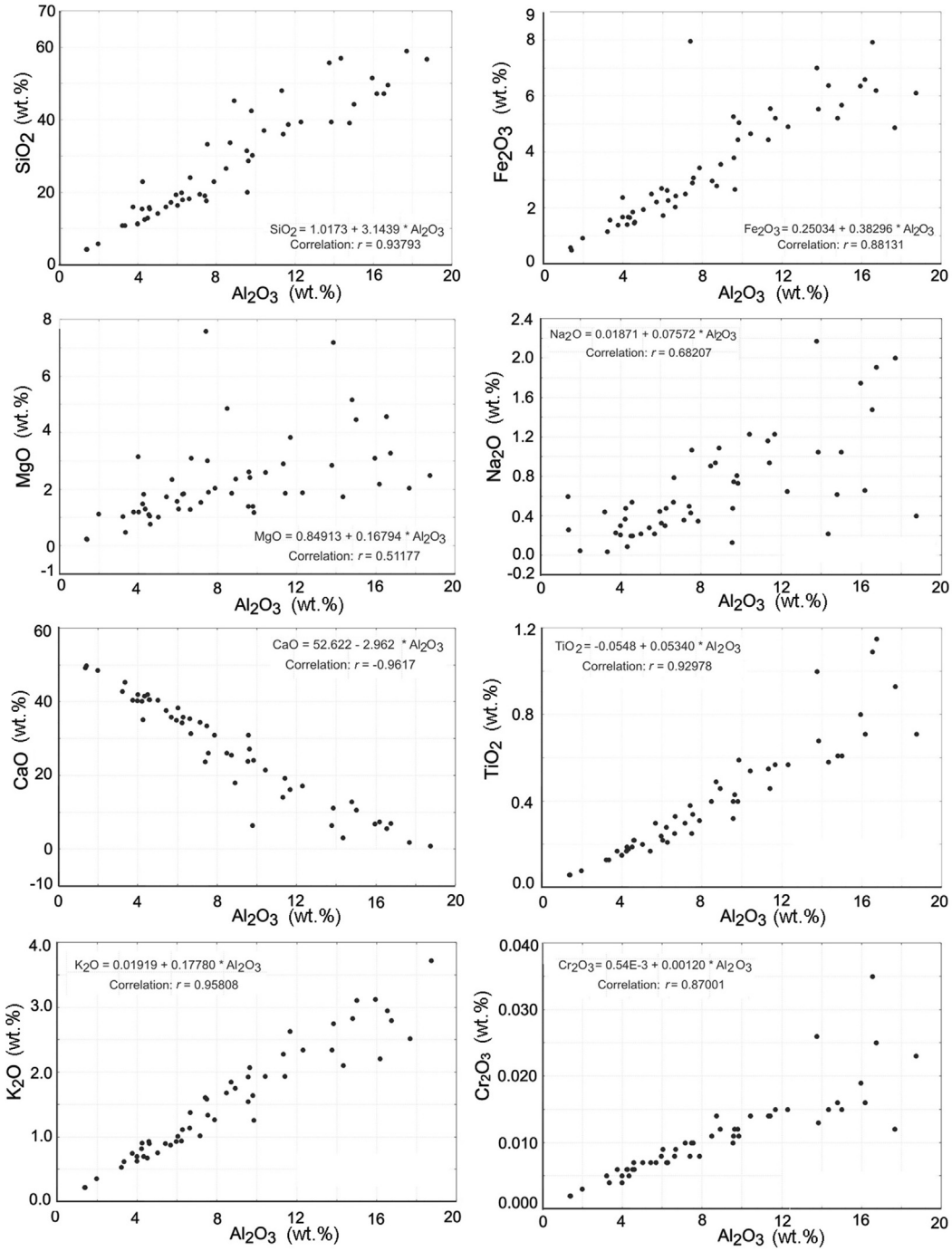

Figure 4. Discrimination plots of major element oxides SiO_2, Al_2O_3, Fe_2O_3, MgO, Na_2O, CaO, TiO_2, K_2O and Cr_2O_3.

quartzose sedimentary rocks and, subordinately, from igneous rocks.

The ratio of SiO_2/Al_2O_3 is used as an indicator of the maturity of sedimentary rocks as well as of the presence of quartz in relation to the clay minerals and feldspar (Cullers, 2000). In most of the samples the ratio of SiO_2/Al_2O_3 was uniformly ≥ 3 (Supplemental Table). Al- and Si-poor minerals like carbonate minerals are causing varied dilution of SiO_2 and Al_2O_3 that produce a constant SiO_2/Al_2O_3 ratio (Cullers, 2000). The ratio of K_2O/Al_2O_3 is significantly different for clay minerals and feldspars, and is used as an indicator of source composition of pelitic sedimentary rocks. For the clay minerals, K_2O/Al_2O_3 ratio is 0–0.3, and for feldspars it ranges 0.3–0.9 (Cox et al., 1995). Pelitic sedimentary rocks with K_2O/Al_2O_3 ratio >0.5 indicate a significant content of alkali feldspar relative to other minerals in the original rocks, while those with K_2O/Al_2O_3 ratio <0.4 suggest recycling of pelitic sedimentary rocks (Cox et al., 1995). In most of the analysed samples this ratio is less than 0.2 (Supplemental Table), therefore they should be derived from older pelitic sedimentary rocks. From the mineral composition of the analysed sediments it could be presumed that the

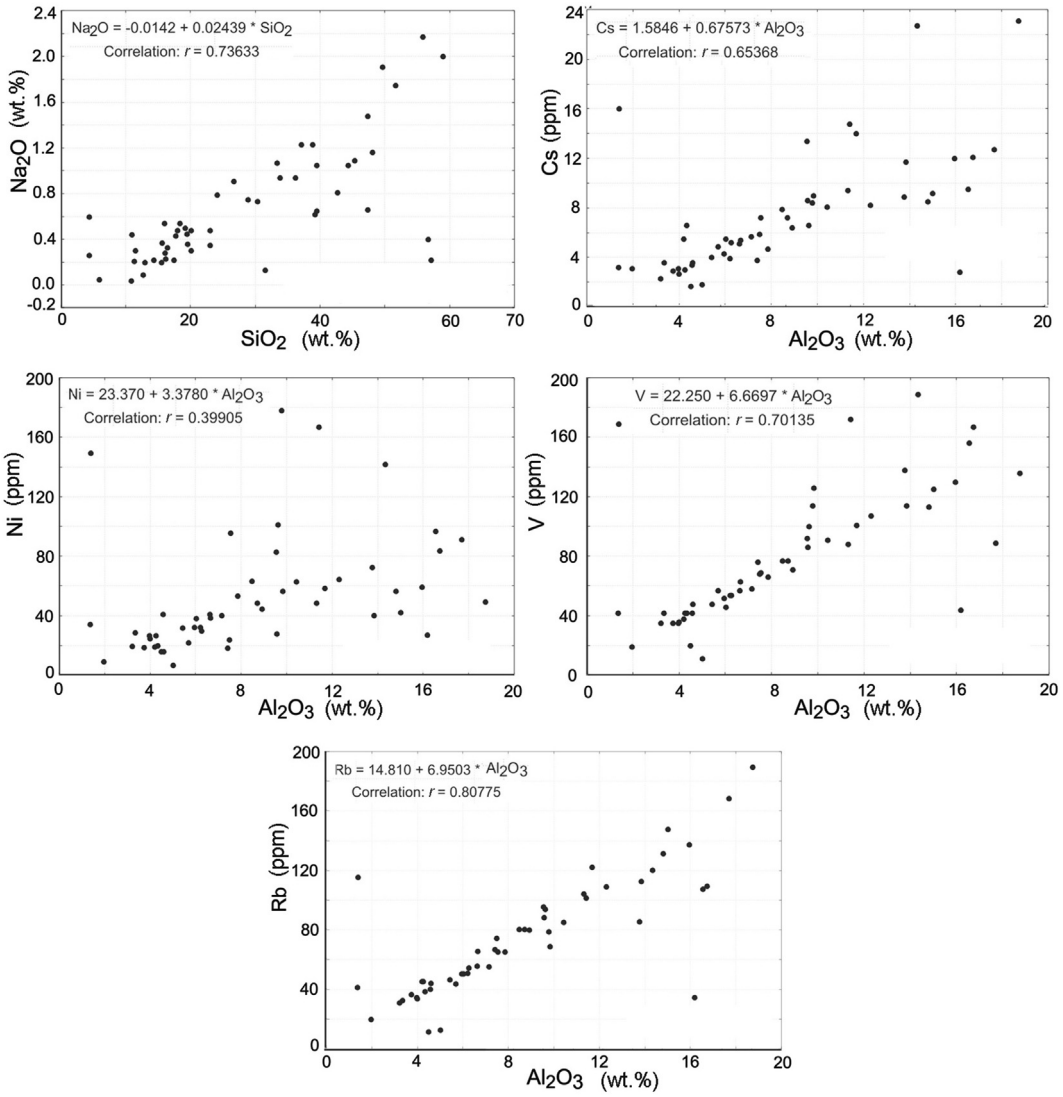

Figure 5. Discrimination plots of major element oxides (SiO_2, Al_2O_3, Na_2O) and trace elements (Cs, V, Ni, Rb).

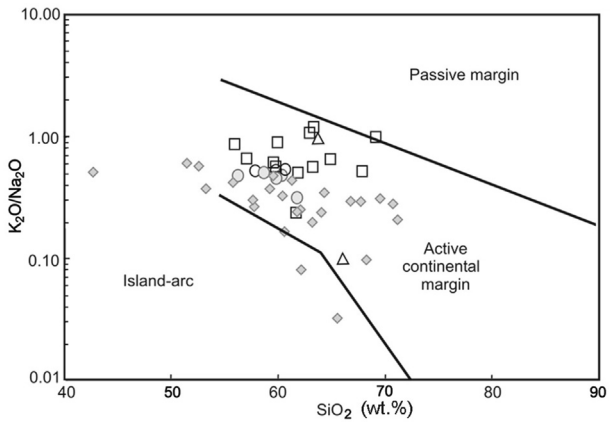

Figure 6. Tectonic discrimination diagram according to Roser and Korsch (1986). Plots for Miocene pelitic sedimentary rocks. Filled rhombs are Sava Depression samples, open squares are Mt. Medvednica samples, filled circles are Požega Sub-depression samples, open circles are Mt. Psunj samples, and triangles are Moslavačka Gora Mt. samples.

potassium content in the samples originates from the presence of illite. Such conclusion is supported by the good correlation of K_2O and Al_2O_3 (Fig. 4).

The Na_2O/K_2O ratio in the analysed samples varies in a wide range from 0.10 to 2.73, which is due to the differences in the mineral composition. The sodium analysed in pelitic sedimentary rocks is related mostly to plagioclase. In the lesser extent it can be related to exchangeable interlayer cations in the clay minerals, while the potassium is mainly associated with illite. Na_2O has good correlation with Al_2O_3 (Fig. 3) and with SiO_2 (Fig. 4). Samples containing plagioclase have a higher ratio of Na_2O/K_2O (Table 2).

Based on the results obtained from the diagram (Roser and Korsch, 1988; Fig. 7) as well as SiO_2/Al_2O_3, K_2O/Al_2O_3 and Na_2O/K_2O ratios (Supplemental Table), one can conclude that the analysed samples are compositionally similar to the upper continental crust (UCC). Furthermore, the source material were predominantly quartz-rich sedimentary rocks and, to a lesser extent, igneous rocks. The samples belong to the mineralogically mature sedimentary rocks.

5.2.2.2. Trace elements. The values of element ratios critical for the provenance such as Eu/Eu*, La/Sc, Th/Sc, La/Co, Th/Co and Th/Cr of

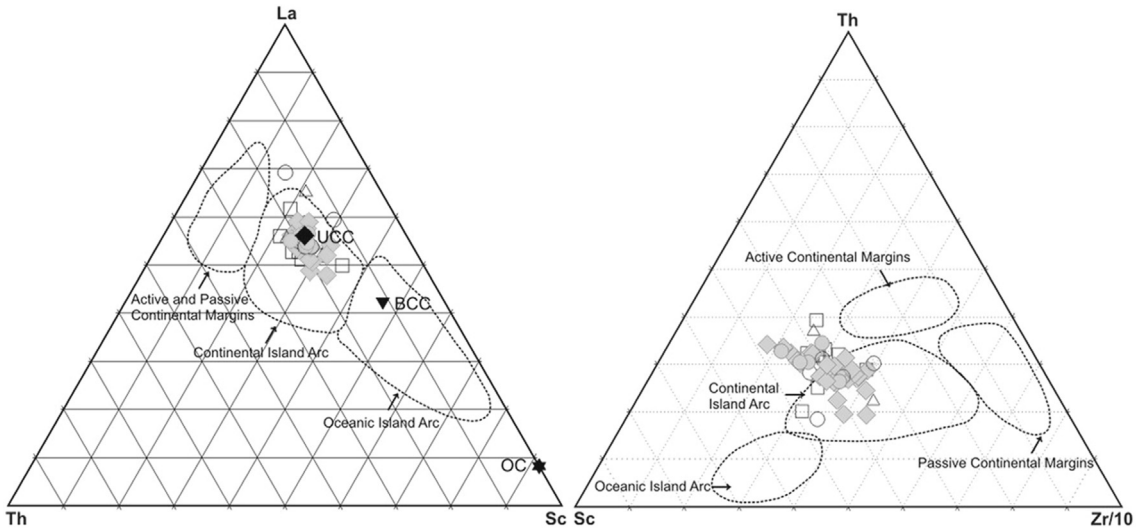

Figure 7. Discrimination plots La-Th-Sc and Th-Sc-Zr/10 for tectonic settings according to Bhatia and Crook (1986) (symbols as in Fig. 5). Average composition of Upper Continental Crust (UCC), Bulk Continental Crust (BCC) and Ocean Crust (OC) (after Taylor and McLennan, 1985) are additionally plotted.

analysed pelitic sedimentary rocks (Supplemental Table), correspond with the values for acid rocks (Cullers, 2000). Eu shows negative anomalies in all analysed samples (Fig. 3). The ratio of Eu/Eu* indicates the size of Eu-anomalies (Cox et al., 1995). There is no fractionation of Eu with regard to other REE during diagenesis and weathering. Therefore, the size of the Eu-anomalies in younger pelitic sedimentary rocks indicates the type of source rocks (McLennan, 1989; Cox et al., 1995). The sum of REE, depending on the carbonate content, varies in the analysed samples from 22 to 184 ppm, while the LREE/HREE ratios are more uniform (LREE/HREE = 5.8–8.9 ppm). In the analysed samples $(La/Lu)_{cn}$ ratio ranges from 6.3 to 10.3. High LREE/HREE and $(La/Lu)_{cn}$ ratios indicate a predominantly acid (Si-rich) source rocks. In the Th/Co versus La/Sc diagram proposed for the differentiation of source rock (Cullers, 2002) (Fig. 9) all analysed samples fall in the area closer to the acidic than the basic rocks. The analysed samples were compared with the upper continental crust (UCC), the average granite and basalt from Middle Oceanic Ridge (MORB) in the diagram Th/Sc–Cr/Th proposed for distinguishing the source rocks (Totten et al., 2000) (Fig. 10). The line in the diagram represents the model created by mixing felsic and mafic components. The diagram shows that the analysed pelitic sedimentary rocks formed mainly by weathering from felsic rocks, while the mafic rock has a lesser share in their formation. The provenance analysis based on the trace elements and REE content indicates that the pelitic sedimentary rocks formed from different rock types, but mostly from acid (Si-rich), or felsic rocks.

5.3. Discrimination function analysis of pelitic samples from different sedimentary environments

A suite of 39 chemical variables were selected as predictor variables in computing the original discriminant model. Since the whole rock composition of the pelitic sedimentary rocks represents a typical example of compositional data where all components

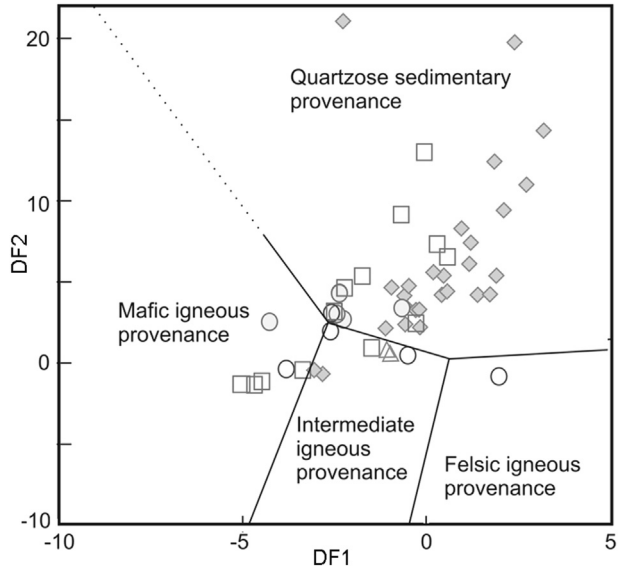

Figure 8. Plot of discrimination functions 1 (DF1) and 2 (DF2) (Roser and Korsch, 1988) showing four provenance groups (symbols as in Fig. 6).

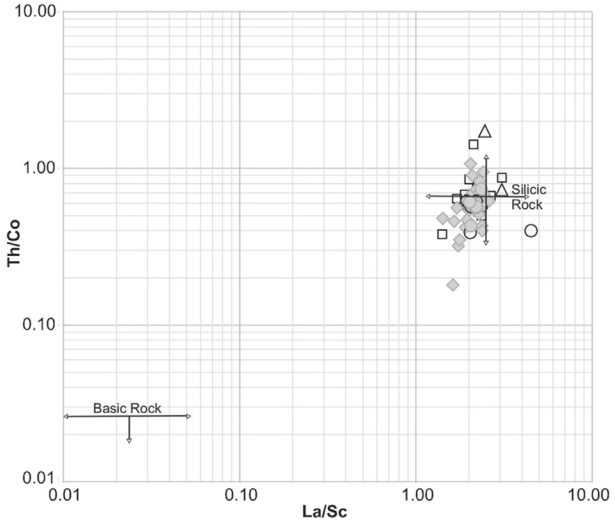

Figure 9. Th/Co vs. La/Sc discrimination diagram (after Cullers, 2002) for Miocene pelitic sedimentary rocks.

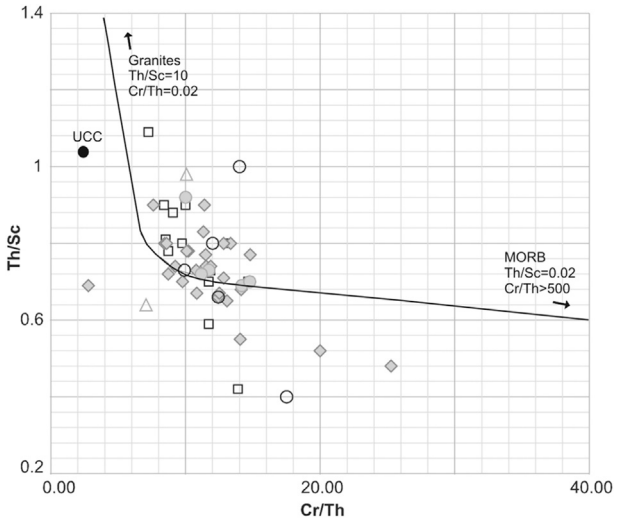

Figure 10. Th/Sc vs. Cr/Th discrimination diagram for Miocene pelitic sedimentary rocks (after Totten et al., 2000).

(variables) sum to a constant value (100%) producing the notorious closure problem in the classical (Euclidean) statistics (e.g. Aitchison and Egozcue, 2005; Buccianti and Pawlowsky-Glahn, 2006; Buccianti, 2013), all data was necessarily transformed prior to execution of the discriminant analysis. The centered log ratio transformations (clr) of the raw (compositional) data was used for translating the data from the "closed" simplex sample space of raw compositions, or parts, (chemical contents) into the well-known algebraic-geometric structure of the unconstrained Euclidean space. Transformation process was executed according to the following equation:

$$clr(x) = \left(\log\frac{x_1}{g(x)},\ \log\frac{x_2}{g(x)},\ \log\frac{x_3}{g(x)},\ \ldots,\ \log\frac{x_D}{g(x)}\right)$$

where x_1, x_2, x_3,…x_D represent parts (compositions), and $g(x)$ represents the geometric mean of the parts.

Discriminant analysis was used in its traditional sense to build a predictive model of a multiple-group discrimination based on the set of predictor variables (clr-transformed quantities of chemical elements in the rock). Four sedimentary environments were selected as a criterion for group separation independent of the measured variables. The results of analysis are highlighted in Table 3 and Figs. 10 and 11.

Table 3 shows the discriminant power of the computed discriminant functions. All three functions are statistically highly significant ($p << 0.05$). However, they are also almost equally important for geological (litho-geochemical) interpretation of the sedimentary environments judging from the comparatively low Eigen value range. The first discriminant function (DF1) makes the greatest contribution to discrimination between the groups accounting for somewhat less than 50% of the total variability. As seen from Fig. 11 it separates the group of freshwater sediments (F) enriched in Cr_2O_3, Zr, TiO_2, Na_2O and Hf from the other three groups that are decreased in these elements. This is in accordance with the fact that freshwater (early Miocene pelitic) sediments are more abundant in siliciclastic material, i.e. contain a lesser amount of carbonate component (Table 2). On the contrary, sediments originated both in marine environment with reduced salinity (MRS) and in brackish environment (B) are enriched in CaO, TOT/C, P_2O_5, Cu, As and Ba. In this case, CaO and TOT/C are associated with the carbonate component while P_2O_5, Cu, As and Ba are probably related to clay minerals. Due to its roughly intermediate position between the F group on the one side and the MRS and B on the other, M group might be said of being a chemical "mixture" of all groups. Accordingly, DF1 can be labeled as a function discriminating between predominantly carbonate and siliciclastic depositional environments (freshwater vs. brackish and marine).

Table 3
Multivariate test for overall significance of discrimination, and test of residual roots.

No. of variables	39
Wilks' lambda	0.00017
Approximate F ratio	4.558
Degrees of freedom	[117; 30]
p-level	$p < 0.000$

DF	Eigen value	Eigen (%)	Canon. R	Wilks' λ	chi^2	df	p-level
1	25.284	46.64	0.981	0.000	256.8	117	0.000
2	17.603	32.47	0.973	0.004	160.3	76	0.000
3	11.326	20.89	0.959	0.081	74.1	37	0.000

The second discriminant axis accounts for almost one third of the groups' variability. Interestingly, it holds a portion of the residual variability left after extraction of DF1, which is associated with the freshwater group (F). Thus, it builds a strong contrast between the F and MRS groups on the one side and marine (M) group on the other. Similarly as in the case of DF1 the brackish group (B) performs neutrally, exhibiting an average chemical composition with respect to DF2. Geochemically, interpretation of DF2 revolves around enrichment of F and MRS groups in Cu, As, Hg, Ni, Mo, Fe_2O_3, V, Co and Cs, and simultaneous deficit in CaO, P_2O_5, MnO, TOT/S, MgO and Na_2O contents with respect to the M group, and vice versa. High positive loadings of trace metals simultaneously with negative loading of TOT/S are somewhat enigmatic indicating the problem with possible presence of sulfide minerals in the former two groups. It was shown earlier (Figs. 4 and 5) that other elements positively loading on DF2, such as Fe_2O_3, V, Co, Cs and Ni, show a good, positive bivariate correlation with Al_2O_3. From the observed mineral composition it is evident that Al_2O_3 is related to clay minerals while the smaller portion in a few samples can be associated with feldspars. This correlation indicates that their content is controlled by proportion of clay minerals. Fe^{3+} and Ga can partly replace Al and Si in tetrahedral layer while in the octahedral layer cations such as Al, Fe, Mg, Mn, Cr, Li, Ti, Zn, Ni and V usually appear (Weaver and Pollard, 1973; Newman and Brown, 1987; Slovenec and Bermanec, 2003). As interlayer cations usually occur K, Cs, Na, NH_4^+, Rb, Ba and Ca. However, trace metals such as Hg, Cu, As, are not included in the structure of clay minerals. There is a possibility that the trace metals are adsorbed on the surface of fine-grained sediments with large specific surface area both by physical and chemical sorption (Siegel, 2002). This, however, may be problematic since K_2O, Na_2O and MgO components are negatively associated with the DF2, together with TOT/S. Based on the mineral analysis, some samples from the F and MRS groups contain an increased amount of ferrous minerals such as pyrite and only one sample contains hematite (Table 2) indicating again that the trace metals marking F and MRS group must be, at least partly, related to Fe_2O_3. As for M group, it is characterized by carbonate component parts such as CaO, MgO, Sr and P_2O_5. Thus only the origin of TOT/S and MnO associated with marine sediments remains unclear.

As seen from Fig. 12 the third discriminant function DF3, in spite of a considerable residual variability (21%), has little to offer in further clarification of the variable-group relationships. Save for the F group, which stands completely alone, the other three groups gather around the axis intersection—a pattern caused by a relatively

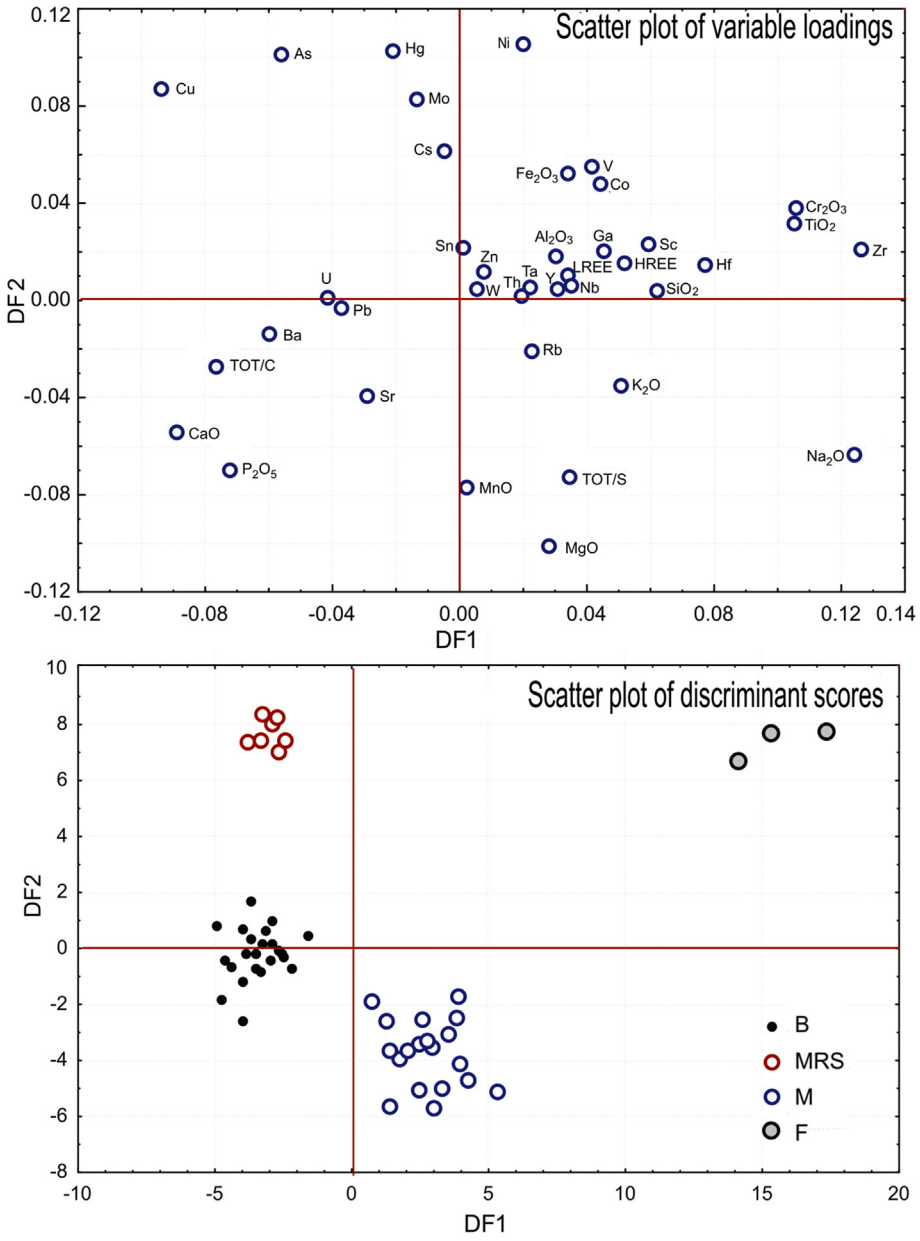

Figure 11. Scatterplot of variable loadings and discriminant scores in reduced discriminant space (DF1/DF2) for Miocene pelitic sedimentary rocks.

small (although statistically significant) geochemical difference among the latter. One can focus only on increased Mo and Ni contents in MRS group.

In studies of possible heavy metal pollution by human activities in fluvial sediments and soils it is necessary to take into account local background values which are influenced by composition of exposed rocks in hinterland and those of underlying the soil respectively (e.g. Grba et al., 2015). Obtained chemical composition data for Miocene pelitic show that in some rocks contents of some elements (Ni, Cr and As) are higher than those stated in the Austrian Standard, ÖNORM S 2088-2 as trigger values for risk assessment regarding human exposure and plant uptake for soil samples.

5.4. Palaeogeography and source areas

The Miocene pelitic sedimentary rocks deposited in the SW part of the PBS consist of carbonate minerals, clay minerals and quartz. Carbonate minerals were mostly precipitated in the basin, or represent fossil remains of organisms with calcareous skeleton, while clay minerals and quartz are of detrital origin. The relative proportion of these components depends on depositional environment, position of source areas, and climate. Lower Miocene pelites contain small amount of carbonate component because freshwater lakes, marshes and alluvial plains which covered the SW PBS at that time, accompanied with sporadically arid climate (Pavelić et al., 2015), were not favourable for precipitation of the carbonate minerals (Fig. 13A). In contrast, the subtropical Central Paratethys Sea and the huge brackish Lake Pannon which existed in the SW PBS during the middle and late Miocene (Fig. 13B and C), together with warm and humid climate (Böhme, 2003), favoured carbonate precipitation and overgrowth of organisms with carbonate skeleton. This is clearly reflected in the increased proportion of the carbonate component in middle Miocene and upper Miocene pelitic sedimentary rocks (Table 2). Clay minerals and quartz grains

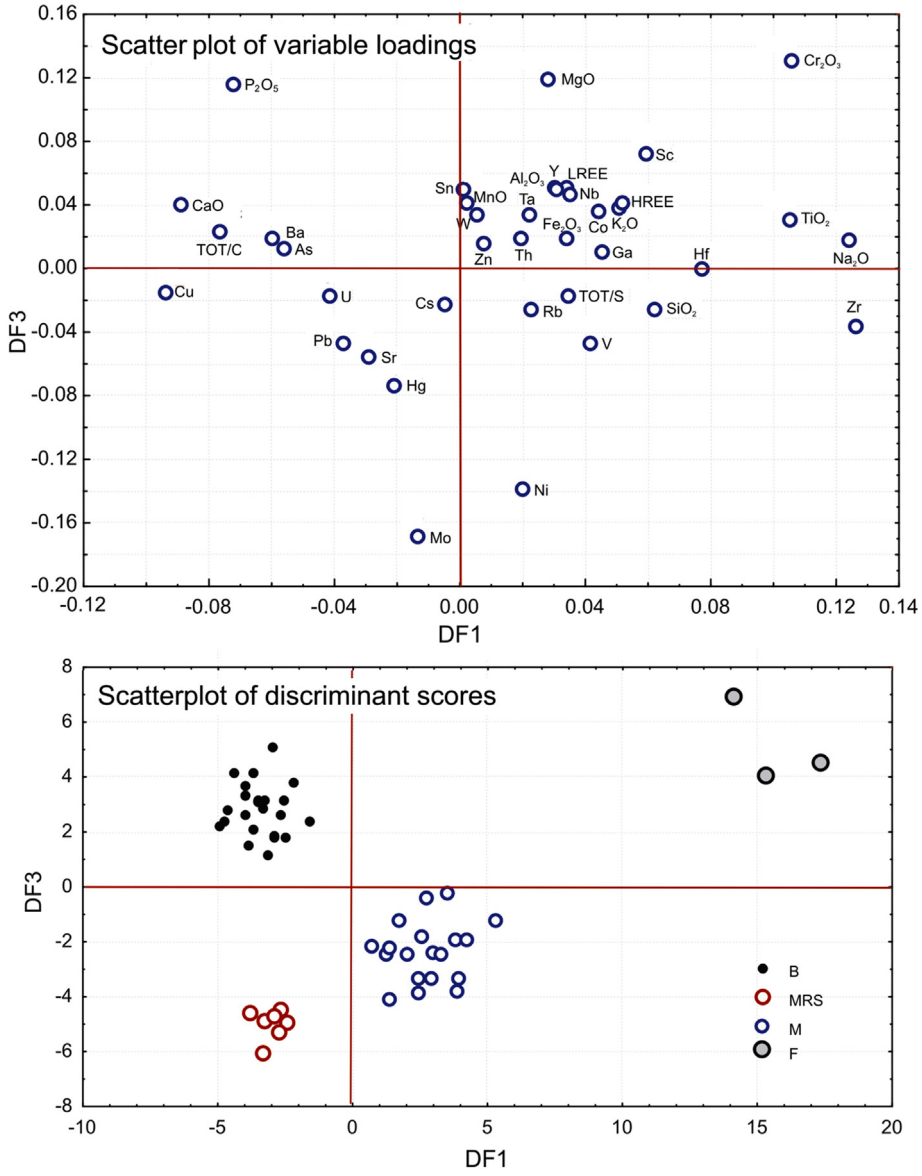

Figure 12. Scatterplot of variable loadings and discriminant scores in reduced discriminant space (DF1/DF3) for Miocene pelitic sedimentary rocks.

in pelitic sedimentary rocks in the SW part of the PBS were mainly sourced from older pelitic sedimentary rocks and quartzose sedimentary rocks, and in smaller amount from felsic magmatic rocks (Fig. 8). These results are in good agreement with provenance analyses of sands and gravels from the same area and the same age (Šćavničar, 1979; Šimunić and Šimunić, 1987; Kovačić et al., 2004; Kovačić and Grizelj, 2006; Grizelj et al., 2007; Kovačić et al., 2009, 2011). According to provenance analyses of middle and course grained clastic detritus, during the early Miocene the main sources of material were located to the south, in the area of the northern Inner Dinarides (Fig. 13A) (Pavelić and Kovačić, 1999; Kovačić et al., 2011). The Inner Dinarides produced a significant amount of clastic detritus during the middle Miocene too, but part of material was derived from locally uplifted blocks in the SW part of the PBS (Fig. 13B) (Kovačić et al., 2011). The upper Miocene clastic detritus is mainly of Alpine–Carpathian provenance, while the supply from the Dinarides or locally uplifted block inside of the SW PBS, was of minor importance (Fig. 13C) (Šimunić and Šimunić, 1987; Kovačić et al., 2004; Kovačić and Grizelj, 2006; Grizelj et al., 2007; Kovačić et al., 2011). The location of the source areas of clay minerals and quartz in the investigated pelitic sedimentary rocks could not be determined on the basis of analyses of pelitic sedimentary rocks, but the similarity in the composition of source rocks of pelitic sedimentary rocks with the source rocks of sands and gravels from the same area suggests their common provenance.

6. Conclusions

The results of the chemical analyses of samples in this study shows that geochemistry of analysed sedimentary rocks is in accordance with their mineralogical composition. No divergence in provenance can be found between the lower Miocene, middle Miocene and upper Miocene sediments based on the chemical composition. Similar chemical composition (major elements and trace elements) of all analysed pelitic sedimentary rocks regardless of their age indicates that they are mostly the product of intensive weathering of different types of rocks. In the case of both the lower Miocene pelitic sedimentary rocks that were the product of

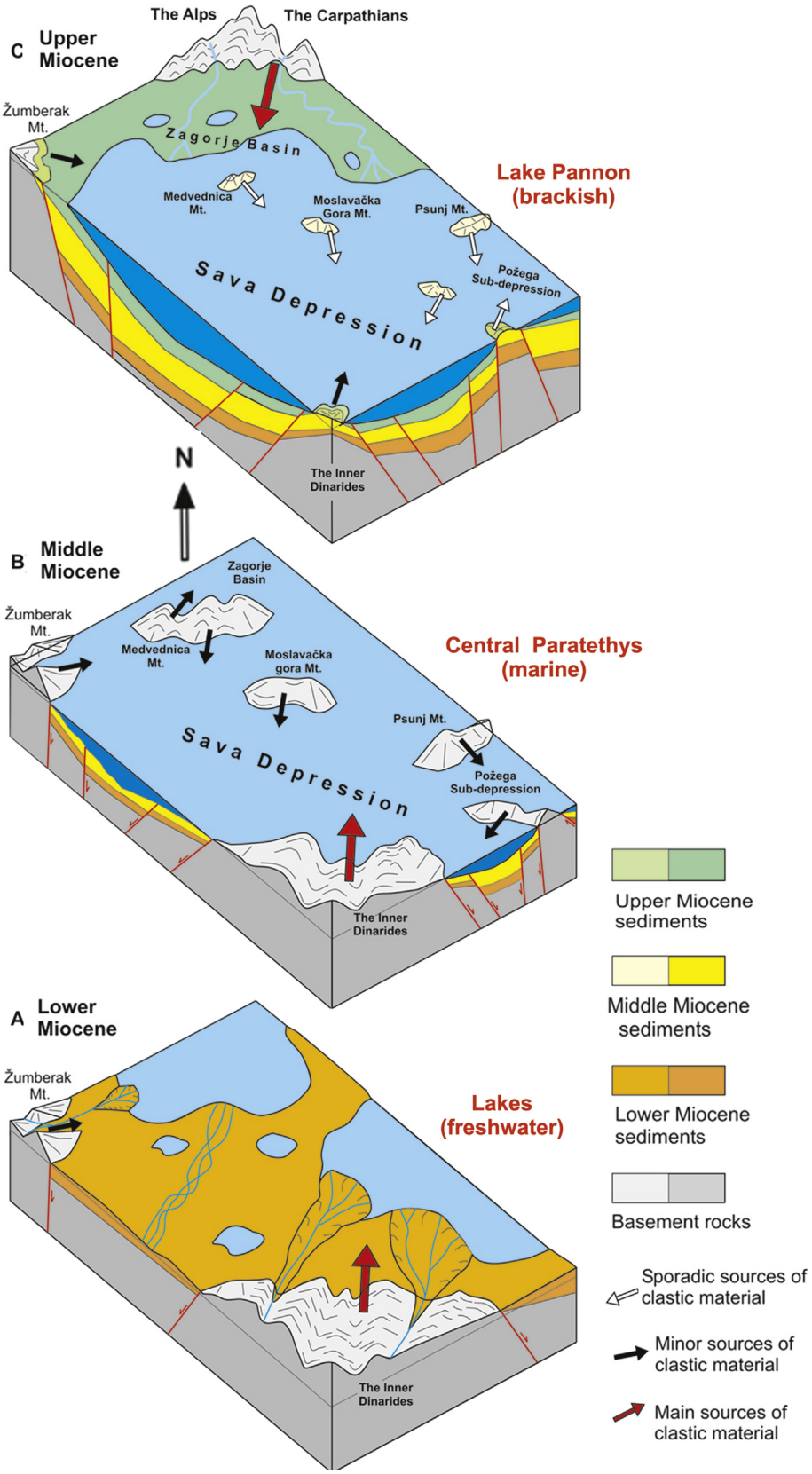

Figure 13. Model of the evolution southwestern part of the Pannonian Basin System. (A) Lower Miocene extension. Deposition pelitic sedimentary rocks in freshwater lakes, marshes and alluvial plains. Main sourced area are the Inner Dinarides and minor Žumberak Mt. (B) Middle Miocene uplifting and erosion of the fault-block crests. Material was deposited within marine environments. Sourced area are the Inner Dinarides and minor local mountains. (C) Upper Miocene deposition in deep brackish Lake Pannon. Main sourced area are the Alps and the Carpathians.

weathering of local uplifted areas, and the upper Miocene pelitic sedimentary rocks whose provenance are Alps and/or the Carpathians, the parent rocks were dominantly “acid” (Si-rich), or felsic rocks. The term “acid” rocks stand for silicic magmatic, older sedimentary and metamorphic rock. Furthermore, the K_2O/Al_2O_3 ratio suggests that Miocene pelitic sedimentary rocks could be recycled older pelitic sedimentary rocks. The analysis of tectonic settings shows the results that are consistent with the role of Pannonian Basin System as one of the Mediterranean back-arc basin. Discriminant analysis based on the sedimentary environment as a grouping criterion is consistent with the analyses based on stratigraphic affiliation.

Obtained chemical composition data for Miocene pelitic sedimentary rocks could provide local background values which are essential in assessment of possible heavy metal pollution in fluvial sediments and soils.

Acknowledgements

This study was funded by the Ministry of Science, Education and Sports, Republic of Croatia, Projects: Basic Geological Map of the Republic of Croatia, 1:50,000 (181-1811096-1093), the Map of Mineral and Energy Resources of the Republic of Croatia (181-1811096-1104), Metamorphic and Magmatic Events in the Pannonian Basin Basement and Dinarides (119-1191155-1156) and Evolutionary Changes of the Dinarides from Subduction to Modern Adriatic Beaches (119-1191155-1159). We would like to thank to anonymous reviewers for their careful revision of the manuscript.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.gsf.2015.11.009.

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